

latter being considered the best though the most expensive. Over the years, Dunlopillo and blown polyester have displaced curled hair from common use in the trade.

Only one company now dresses horsehair in the UK and only a handful in Europe. The Managing Director of the British company sees horsehair as a "traditional and specialized product with certain qualities which synthetic fiber and bristles do not possess and which are needed by a limited number of clients." As to the future, he says: "It is unlikely that new companies will enter the field since the craft skills are by no means easy to acquire. Horsehair, it seems, is thus a product with a restricted but demanding market where customers have a very clear appreciation of the product."

See also: *Fibers and Textiles: An Overview*; *Materials of Biological Origin: An Overview*

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R. H. Gould
[Glemsford, UK]

Hot Isostatic Pressing: Developments in Theory

Hot isostatic pressing (HIP) is rapidly attaining the position of the leading hot consolidation process for metal and, especially, ceramic powders. In addition, healing of casting defects and diffusion bonding have become important applications of the HIP process. Presses with large working spaces (2 m high, 1 m diameter) are now available and are expected to increase productivity and to extend applications outside aerospace and defense.

This article supplements the articles *Hot Isostatic Pressing*, *Hot Isostatic Pressing of Advanced Ceramics* in the Main Encyclopedia, which describe basic HIP practice. The powder is filled into a preform (a "container" of the desired shape) and placed in the pressure vessel; a gas pressure is then applied to the powder compact and the temperature raised. At present there is no systematic way of preselecting the process variables (pressure, temperature, processing time, etc.) to give optimal results. Another critical task is the design of the powder preform. HIP con-

ditions and preform geometry are now found largely by expensive "trial and error" runs.

In recent years, major advances have been made in the basic understanding of the HIP process. The progress (described below) refers to two important aspects of powder consolidation by HIP: the micro-mechanisms of particle deformation leading to densification of the compact (Sect. 1), and the prediction of the final shape of the HIP product by finite element methods (Sect. 2). Both approaches provide a rational basis for selecting HIP parameters and for preform design and thus can help utilize the full technical and economic potential of hot isostatic pressing.

1. Micromechanisms of Powder Densification by HIP

1.1 Modelling

The HIP of powders is a complex process by which a loose aggregate of powder particles is compacted into a dense and strong solid by the simultaneous application of pressure and heat (Exner and Arzt 1983). Several processes can lead to a reduction of the pore volume under pressure:

- (a) particle fragmentation and rearrangement,
- (b) deformation of the zones of contact between particles until closed porosity is formed, and
- (c) shrinkage of individual pores.

Process (a) can only make a transient contribution to the densification of the compact and is therefore usually ignored. When an external pressure is applied to packed powder particles, it is transmitted through the powder bed as a set of forces acting across the particle contacts. The local contact force per unit contact area is defined as the "effective pressure"; it drives localized particle deformation which leads to progressive densification of the powder compact. Because of the stress concentration at the initially small contact areas, the "effective pressure" far exceeds the externally applied pressure at first. During further densification, however, two important effects occur: the areas of contact between neighboring particles grow in size and additional contacts are created as the powder compact shrinks (Arzt 1982). Both processes lead to a continuous reduction in driving force for further densification. This effect, which is termed "geometrical hardening" of the powder compact, explains why initial densification is rapid compared with the removal of the last few percent of porosity.

At the high temperatures employed in HIP, the deformation of the particle contacts under the action of the effective pressure can be due to several micro-mechanisms (see Fig. 1). Initially, the effective pressure is sufficient to cause instantaneous plastic yielding

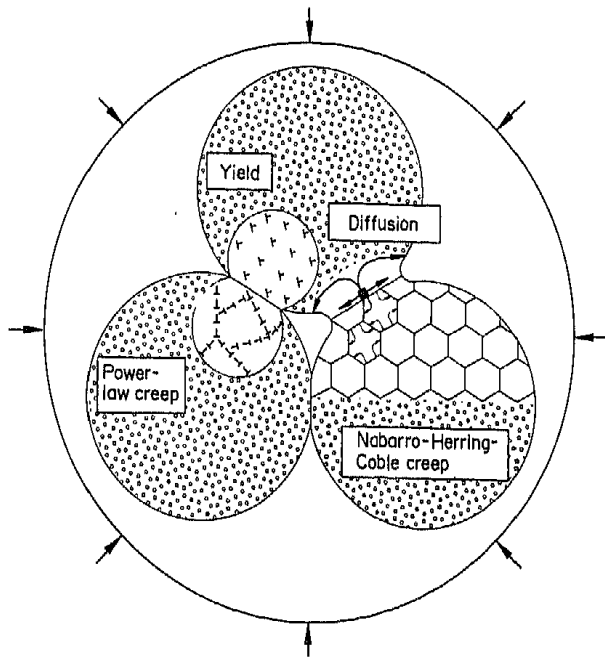


Figure 1
Micromechanisms of particle deformation during hot isostatic pressing

of the contact zone (this is also the only densifying mechanism available during cold precompaction which is often carried out before HIP to improve the thermal conductivity of the powder mass). The resulting contact-flattening leads to a rapid attenuation of the effective pressure until yielding stops. Then, time-dependent deformation mechanisms determine the rate of further densification. One possible mechanism is power-law creep in the contact zone; the microscopic mechanism for this process is known to be time-dependent dislocation activity. The alternative lies in a stress-directed diffusion process, in which atoms can diffuse from the contact area to the pore surface (as, incidentally, in pressureless sintering) or, if the powder particles are polycrystalline, they can deform by appropriate atom diffusion over the length of a grain diameter (Nabarro-Herring-Coble creep). Nondensifying mechanisms, such as surface diffusion or vapor transport, which are not enhanced by the applied pressure, can be neglected.

For these HIP mechanisms, constitutive equations have been developed which predict the contribution of each mechanism to densification. They are based on expressions describing the evolution of the effective pressure and on the physical principles of the high-temperature deformation mechanisms mentioned above. In order to allow a stringent mathematical treatment, certain simplifying assumptions have to be made. The powder particles are taken as spheres which are arranged in a random dense packing and the HIP parameters, pressure P and temperature T , are assumed to have reached steady-state values, any pressurization and heating effects being

Table 1
HIP equations (after Li et al. 1987)

| Parameter | Function | Conditions |
|-----------|--|---|
| K_i | $\frac{5.6\delta D_b \Omega P}{kTR^3}$ | grain-boundary diffusion ($D < 0.9$) |
| | $\frac{270\delta D_b \Omega P}{kTR^3}$ | grain-boundary diffusion ($D \geq 0.9$) |
| $f_i(D)$ | $\frac{5.6D_v \Omega P}{kTR^2}$ | lattice diffusion ($D < 0.9$) |
| | $\frac{270D_v \Omega P}{kTR^2}$ | lattice diffusion ($D \geq 0.9$) |
| $f_i(D)$ | $5.3 \frac{\dot{\epsilon}_0}{\sigma_0^n} P^n$ | power-law creep ($D < 0.9$) |
| | $1.5 \left(\frac{\dot{\epsilon}_0}{\sigma_0^n} \right) \left(\frac{3}{2n} P \right)^n$ | power-law creep ($D \geq 0.9$) |
| $f_i(D)$ | $\frac{1}{(D - D_0)^2}$ | grain-boundary diffusion ($D < 0.9$) |
| | $(1 - D)^{1/2}$ | grain-boundary diffusion ($D \geq 0.9$) |
| $f_i(D)$ | $\frac{1}{(D - D_0)}$ | lattice diffusion ($D < 0.9$) |
| | $\left(\frac{1 - D}{6} \right)^{1/3}$ | lattice diffusion ($D \geq 0.9$) |
| $f_i(D)$ | $\frac{(D^2 D_0)^{1/3} (D - D_0)}{[9D^2 (D - D_0)]^n}$ | power-law creep ($D < 0.9$) |
| | $\frac{D(1 - D)}{[1 - (1 - D)^{1/n}]^n}$ | power-law creep ($D \geq 0.9$) |

ignored. Shrinkage is assumed to be isotropic. For each mechanism, the constitutive equation thus obtained has the following form (Helle et al. 1985):

$$\left(\frac{dD}{dt} \right)_i = K_i f_i(D) \quad (1)$$

where dD/dt is the derivative of the relative density D (density divided by theoretical density) with respect to time t , K_i is a kinetic constant which contains the HIP parameters and the material properties and $f_i(D)$ is a purely geometrical function dependent only on the actual relative density D . The expressions for K_i and $f_i(D)$ are given in Table 1. D_0 is the initial relative density, $\dot{\epsilon}_0$, σ_0 and n are the power-law creep parameters: $\dot{\epsilon} = \dot{\epsilon}_0 (P/\sigma_0)^n$, D_v is the volume diffusivity, δD_b is the grain-boundary thickness multiplied by the grain-boundary diffusivity, Ω is the atomic volume, R is the powder particle radius and k is Boltzmann's constant.

1.2 HIP Diagrams

For optimizing HIP parameters, information about the dominant densifying mechanism can be important. According to Eqn. (1), the competition among the mechanisms depends in a complicated way on the powder and material properties, for example, powder particle size, grain size, diffusivity, creep parameters and the HIP parameters (HIP pressure and temperature). In order to illustrate these dependencies, theoretical "HIP diagrams" have been constructed for a number of materials. Example are shown for tool steel (Fig. 2) and alumina (Fig. 3). Further diagrams are available for superalloys, copper and silicon nitride (Arzt et al. 1983, Helle et al. 1985).

HIP diagrams show the field of dominance of each mechanism (that is, the range of pressure or temperature and density in which a given mechanism contributes more to the densification rate than the others). The field boundaries are the lines along which two mechanisms contribute equally to the total. Superimposed on the fields are contours of constant time; they predict the HIP processing time necessary for reaching a given compact density. Where available, experimental HIP conditions are shown on the diagrams as data points. Comparison between theory and experiment is usually favorable, but it must be remembered that such HIP diagrams

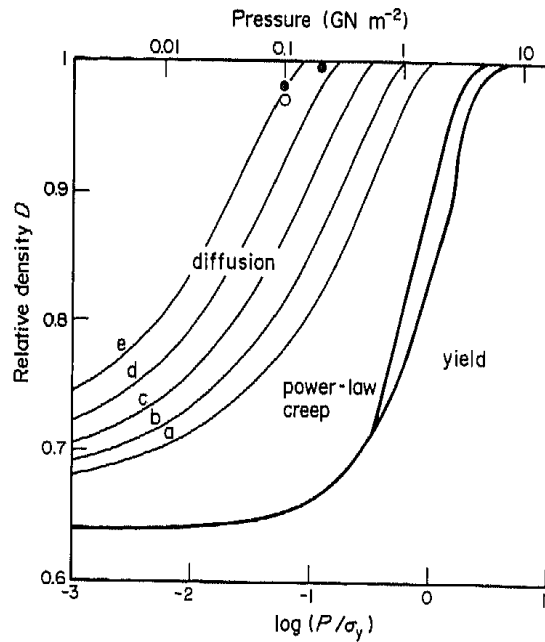


Figure 3
HIP diagram for Al_2O_3 with a particle size of $2.5 \mu m$, at a temperature of $1200^\circ C$. The heavy lines are the field boundaries and the thin lines are contours of constant time: a, 0.25 h; b, 0.5 h; c, 1 h; d, 2 h; e, 4 h. ●, 4 h; ○, 2 h (experimental data) (after Arzt et al. 1983. © American Society for Metals, Metals Park, Ohio. Reproduced with permission)

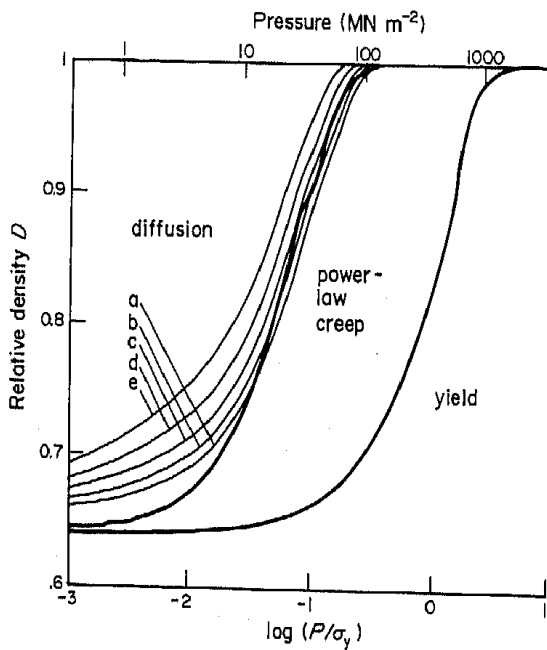


Figure 2
A theoretical density-pressure diagram ("HIP diagram") for a typical tool steel powder with a particle diameter of $100 \mu m$, at a temperature of $1200^\circ C$. σ_y is the yield stress of the powder material. The heavy lines are the field boundaries and the thin lines are contours of constant time: a, 0.25 h; b, 0.5 h; c, 1 h; d, 2 h; e, 4 h (after Arzt et al. 1983. © American Society for Metals, Metals Park, Ohio. Reproduced with permission)

are based on "average" material parameters which can be subject to considerable batch-to-batch scatter. A precise HIP diagram can be constructed only by careful data selection and iteration with selected HIP cycles.

Such HIP diagrams give considerable insight into the HIP process. Figure 2, for example, shows that the initial densification in a packed powder is always a result of plastic yielding (in practice, this stage is usually traversed by cold precompaction to increase the thermal conductivity of the powder mass). Then at intermediate densities a region in which power-law creep dominates is usually encountered. Final densification at medium pressure is mainly due to diffusional mechanisms. The extension of the mechanism fields depends on the HIP parameters: at relatively low pressure, the diffusion mechanisms tend to contribute more to densification than power-law creep which in turn predominates at high HIP pressures. This is because the driving force for the diffusion processes is much less sensitive to the effective pressure than the rate of dislocation creep. Similar diagrams shed light on the role of the powder properties during HIP. Unlike power-law creep, the diffusional processes depend critically on the powder particle or grain size. Therefore in fine, polycrystalline powder particles, these mechanisms will be favored over power-law creep.

One complication for the diffusional mechanism is the fact that it depends on the presence of a grain

boundary, which must act as a source for atoms. High-temperature exposure of the compact during HIP can result in grain growth and pore separation from the boundaries, isolating the pore in midgrain. The diffusion mechanism is then rendered inoperative and power-law creep, which is insensitive to such a microstructural change, will extend to higher densities. This effect has been incorporated in recently refined versions of the HIP diagrams (Helle et al. 1985).

Powders of different material classes require quite different HIP parameters and they densify by different mechanisms. The comparison between tool steel (Fig. 2) and alumina (Fig. 3) is instructive: the power-law creep field disappears almost completely in the ceramic material and densification is effected mostly by diffusion. This is because the dislocation activity necessary for creep is impeded by the covalent atomic bond (another reason is the much finer particle size of ceramic powders). For such a material, cold precompaction does not produce much densification as pressures in excess of 1 GPa are required to produce significant densification by yielding alone.

In addition to giving information on densifying mechanisms, HIP diagrams can provide a tool for selecting optimal conditions for commercial HIP cycles. They can help cut down the number of expensive trial and error runs. For example, Fig. 4 illustrates the trade-off, predicted theoretically, of HIP temperature and pressure for various materials. The line for the ceramic material is much steeper than for metallic alloys, indicating that raising the temperature (rather than the pressure) should be the

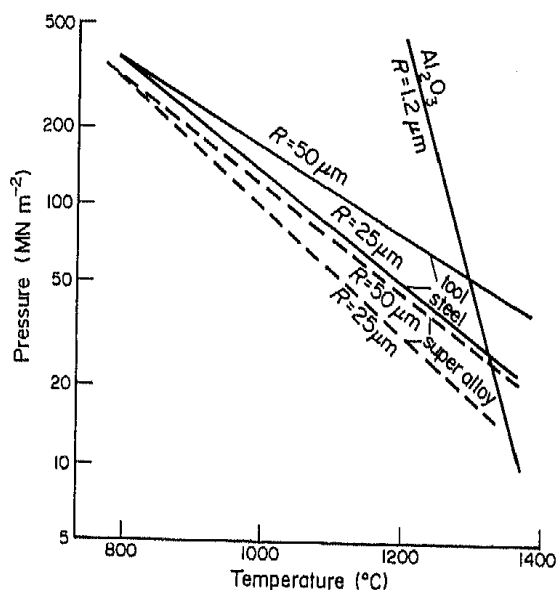


Figure 4
A pressure-temperature HIP diagram, showing the combination of P and T required to achieve a relative density of 0.99 in 1 h (after Arzt et al. 1983).
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best way to reduce processing times (assuming that times are not already limited by thermal conduction into the compact).

2. Prediction of Final Shape

During the HIP process, the volume of the powder compact decreases by up to 30%. Ideally, the shrinkage should be isotropic so that the shape of the hot isostatically pressed product is identical to the preform before HIP, differing only in scale. In practice, inhomogeneous densification can lead to substantial distortions which must be allowed for in preform design. Therefore, the prediction of the final shape is essential for producing HIP components of near-finished dimensions ("near-net-shape technology").

Inhomogeneous densification can be caused by imperfect HIP practice, for example, nonuniform filling of the preform, thin spots in the preform material or incomplete outgassing. Even if these problems are avoided, shape distortions can occur because the HIP parameters temperature and pressure are not constant over the dimensions of the compact. Heat flow through a powder is slow and under normal HIP conditions temperature gradients are inevitable. As heat diffuses into the powder, the hotter surface layers densify faster than the interior and this results in a dense skin. Heat is conducted through the denser skin faster than through the less-dense center, further adding to the temperature difference between the surface and the interior. Under certain conditions, a densification front develops and propagates inwards, leading to large shape changes of the compact.

A numerical analysis of the coupling between heat flow and densification (Li et al. 1987) shows that the dimensionless variable

$$C^* = K_1 X_m^2 / a_s \quad (2)$$

characterizes the tendency to shape distortion. The variable C^* measures the ratio of the rate of densification (proportional to K_1 , see Eqn. (1)) to the rate of heat flow (measured by $a_s X_m^{-2}$, where a_s is the thermal diffusivity of the powder material and $2X_m$ is the linear dimension of the powder compact). When $C^* \ll 1$, densification is nearly uniform, but for $C^* \gg 1$, a densification front develops: the surface displacements are then nonuniform and dramatic shape changes can occur.

Another consequence of nonuniform densification is that after cooling to ambient temperature, residual tensile stresses can develop at the surface of the HIP product. Brittle ceramic materials with low a_s are particularly susceptible to such problems. The mathematical analysis can help to define preheating times before pressurization and/or limitations in component dimensions in order to minimize the effects of inhomogeneous densification owing to temperature gradients.

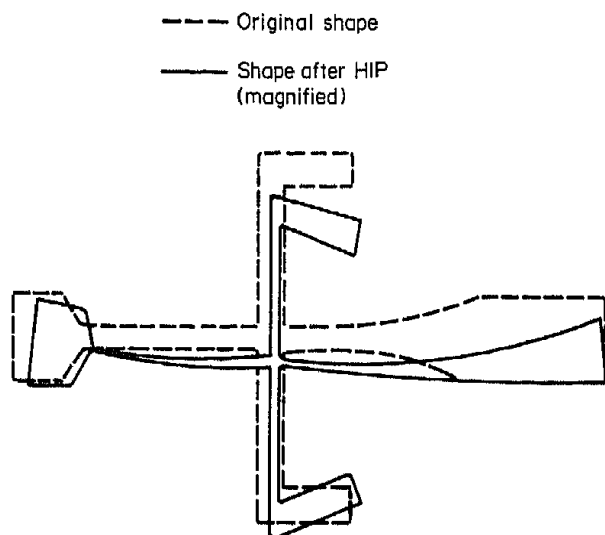


Figure 5
Predicted shape distortions during HIP of a compressor disk model based on a finite element analysis. The displacements are amplified for clarity (after Cassenti 1982. © American Institute of Aeronautics and Astronautics, New York. Reproduced with permission)

Inhomogeneous loading is another source of shape distortions during HIP. It can be caused by gravitational effects to which the powder particles are subjected, to temperature differences between the preform and the powder and to variations in the stiffness of the preform (for example, at corners). Nonlinear finite element codes have been designed, which take these effects into account by modelling both preform and powder deformations during HIP (see, for example, Cassenti 1982). These codes are based on constitutive equations from continuum plasticity theory incorporating yield and creep. The final shape prediction of an actual HIP turbine disk is shown in Fig. 5: the deformed shape illustrates clearly the effects of gravitational loading. The finite element analysis predicts an increase of the radius of the inside hole and a shrinkage of the outer radii, both of which were experimentally observed. By allowing parametric studies to be performed, such computer programs are invaluable tools for preform design and will help realize the full potential of near-net-shape technology in HIP.

See also: Hot Isostatic Pressing; Hot Isostatic Pressing of Advanced Ceramics; Powder Mechanics (Suppl. 1); Rapid Quenching from the Melt: Formation of Metastable Crystalline Phases (Suppl. 1)

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E. Arzt
[Max-Planck-Institut für Metallforschung,
Stuttgart, FRG]

Hugoniot Curve

W. Rankine (1870) and J. Hugoniot (1889) showed more than a century ago that a shock wave or shock front (a high-pressure wave) advancing through a material creates a discontinuity in density, pressure and temperature. This discontinuity advances with a velocity which corresponds to the maximum pressure of the shock pulse. Such shock pulses can originate by a rapid displacement generated by a high-velocity impact or an explosive charge. Rankine and Hugoniot actually developed a system of equations which in principle describe the conservation of mass, momentum and energy in the high-pressure states of materials undergoing shock-wave compression. This compression, even in the case of uniaxial or plane shock waves, is considered to be ideally hydrostatic if the peak pressure is sufficiently high.

1. Conditions at a Shock Front: Rankine-Hugoniot Equations

The calculation of shock-wave parameters, and determination of dynamic conditions in materials subjected to strong shock pulses, are based on the assumption that materials subjected to high shock pressures (in excess of the so-called dynamic yield stress of the material) behave like compressed liquids, and that hydrodynamic theory is therefore applicable.

A shock pulse as depicted in Fig. 1, which propagates through a material (especially a metal or alloy), can be represented schematically by a planar shock front which separates the material into two states or regimes. The disturbance corresponding to the shock front (which might ideally have some thickness) propagates with a velocity U_s (the shock velocity) into an initially undisturbed (uncompressed) state (having a density ρ_0 , an internal energy E_0 and a corresponding pressure P_0 which in relation to the pressure P of the shock pulse behind the shock front is usually negligible (or zero)). In the high-pressure region behind the shock front (Fig. 1) the material

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